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54 TITLE OR SUBJECT OF THE APPLICATION

METHOD FOR SEPARATING COMPONENTS FROM A RAW MATERIAL CONTAINING NEUTRAL COMPOUNDS OF TALL OIL SOAP FROM BLACK LIQUOR THROUGH SHORT PATH DISTILLATION AND THE EXTRACTION OF STEROLS, STANOLS OR FATTY ALCOHOL COMPOUNDS

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57 SUMMARY

A procedure for the separation of the unsaponifiable components of black liquor soaps from the cellulose industry is disclosed. The unsaponifiable components undergo distillation in one or more short path distillation columns at temperatures between 100 to 250°C and pressure between 0.01 to 5 mbar to give rise to fractions containing essentially free sterols and stanols; sterol, stanol and fatty alcohol esters; and free fatty alcohols such as docosanol and tetracosanol. The procedure is highly efficient and allows of the extraction of concentrates of the different fractions of great purity, suitable for human use and consumption or as raw material for the food, pharmaceutical and cosmetics industries.

Pursuant to Art. 44 of Law No. 19.039 on Industrial Property, I/we state that the data entered on this form are true.	IPD Office Use **RECEIPT**

This invention involves a process for fractioning unsaponifiable material from black-liquor soaps in the cellulose industry, a process whereby fractions containing essentially free sterols, fatty alcohols, and sterol and fatty alcohol esters, respectively, are separated from each other. The fractions containing sterols or fatty alcohols may be used as such in the food, cosmetics or pharmaceutical industries or they can be used as raw materials to be transformed into other products in great demand.

BACKGROUND

General

Origin, composition and uses of black-liquor soaps

Black-liquor soaps are a sub-product of the Kraft pulping process with pinewood or other woods. Typically, in the Kraft process, wood chips are digested for two hours at 170°C in aqueous liquor containing sodium hydroxide and sodium sulfide. The digestion delignifies the wood and gives rise to a dark-colored aqueous suspension called black liquor, which, in addition to lignin, contains cellulose pulp, sodium and resin acid and fatty acid soaps, a series of neutral organic products, such as sterols, terpenes, fatty alcohols, sterol and fatty alcohol esters, and products from the decomposition of lignin. Under these conditions, the cellulose is stable and remains in suspension in the black liquor. When the pulping reaction is completed, the cellulose pulp is separated from the black liquor and washed. The pulp may be used as such or undergo subsequent purification processes.

The black liquor must be recovered for both environmental and economic reasons. To this end, the liquor typically is concentrated by evaporation to a black liquor solid content of approximately 23-32% in weight, from which the fatty and resin acid soaps are separated out, together with a series of hydrophobic or neutral compounds made soluble in these soaps and which become concentrated in the top of the container, from where they are removed or skimmed. This fraction is referred to in the English-language technical literature as "skimming," which is the term that we will use as synonymous with "black-liquor soaps." Other

names used for that fraction are "tall-oil soap" or also "CSS," from the acronym in English for the expression, "Crude Sulphate Soap."

The skimming generally contains between 30 to 50% of water. The solid material is a complex mixture of sodium fatty soaps and sodium resin soaps and a series of hydrophobic substances essentially consisting of sterols, stanols, fatty alcohols, diterpenoids, and sterol and fatty alcohol esters with fatty acids. These hydrophobic compounds, which together make up the neutral unsaponifiable fraction, which is called "unsaps" in the theoretical literature can sometimes comprise up to 25% of the skimming solids.

Sometimes the skimming is used as a fuel, with its calorie power being a little less than half that of fuel oil. Another use is for it to be transformed into tall oil. This is done by adding sulfuric acid and separating the oil formed in the aqueous phase. This oil is known in the technical literature as CTO (crude tall oil). CTO subsequently undergoes a series of vacuum distillations, which produce fatty acids (TOFA or tall oil fatty acids, which are one of the CTO fractions of greatest value), rosin acids (TOR or tall oil rosins), distilled tall oil (DTO), which have a variety of uses and applications, and pitch, the English language name for the bottom of the distillation, used as a fuel or in the preparation of asphalt emulsions.

Until a short time ago, the primary reason for refining the skimming, i.e. separating its unsaponifiable fraction, was to improve CTO quality.

Currently, there is a revaluation of unsaps themselves as a source of important chemical products, such as sterols, stanols, superior alcohols, notably docosanol and tetracosanol and their respective esters, which are finding a growing application in the pharmaceutical, cosmetic and food industries.

The procedures for refining soaps or extraction of neutral or unsaponifiable materials are widely known in the state of the art and consist, without exception, of the extraction of unsaponifiable material with various organic solvents, including extraction with supercritical

solvents and are relatively optimized. On the other hand, procedures for the fractioning of such unsaps present a number of technical as well as economic disadvantages.

Known methods for the fractioning of skimming unsaps

The average chemical composition of the unsaps used in this invention, deriving from domestic cellulose industry skimmings, is indicated in Table I.

The group of components known as "other" consists for the most part of terpenoids (mono and diterpenes and their derivatives) and betulaprenols and an additional series of compounds currently insufficiently characterized.

Most identified components in the unsaps indicated in Table I are compounds of commercial interest. Sterols, whether free or esterified, have different uses as raw materials for the pharmaceutical, cosmetic and fermentation industries for their transformation into steroids. Especially relevant are the esters of sterols and stanols. The former are important anti-tumoral agents, as disclosed in US Patent No. 5,270,041. Stanols, which are the reduced form of sterols, have an important application in the formulation of diets for the reduction of plasma cholesterol levels. The use of free stanols for that purpose is disclosed in US Patent No. 5,244,887, while the use of stanol esters for the same purpose is disclosed in US Patent No. 5,502,045.

Insofar as the fatty alcohols, especially docosanol and tetracosanol, there is growing interest due to their notable pharmacological properties as anti-inflammatory and anti-viral agents. The use of such alcohols for pharmacological purposes is disclosed in numerous U.S. patents, by way of example, US Patents Nos. 4,874,794; 3,031,376; 5,534,554; 5,071,879; and 5,166,219.

Table I

Unsaps average composition

Compound	% weight
3,5- sitostadiene -3-ona	0.6
4-stigmasten-3-ona	0.5
alpha-sitosterol	0.6
beta-sitostanol	7.5
beta-sitosterol	21
campestanol	0.6
campesterol	2.1
cycloartenol	0.5
docosanol	4.4
eicosanol	3.6
ergosterol	0.2
squalene	1.6
fatty alcohol esters	6.1
sterol esters	13.7
hexacosanol	0.2
methyl-encycloartenol	0.4
pimaral	0.7
pimarol	2.1
stigmasta-3-ona	0.3
tetracosanol	2.5
others	30.8

The methods currently known for the separation of valuable components of unsaps deriving from black-liquor soaps or skimming are, almost without exception, different variants of dissolution and re-crystallization. One of the disadvantages of this technique is that it only allows for the recovery of free sterols, leaving in the mother liquor valuable fatty alcohols and alcohol and sterol esters, which practically cannot be fractioned in turn due to the liquor's re-crystallization. This way not only the valuable fatty alcohols, but also the sterol esters are not used, which deprives the sterol preparation obtained by the methods known to the state of the art of an important sterol, which is found fundamentally in sterified form in the unsaps (stigmasterol), and of an appreciable amount of stagmastanol or sitostanol, which recent studies identify as one of the most active and important sterols for reducing plasma cholesterol levels, as disclosed in patent application PCT/CA95/00555 and US No. 5,502,045.

To illustrate the foregoing, the sterol composition in the unsap fraction comprised of esters is indicated in Table II. By means of the procedure of this invention, which is described below, such esters have been separated from the rest of the unsaps, they are then hydrolyzed as described below, and undergo chromatographic analysis with the results shown:

Table II

Relative composition of esterified sterols present in the unsap

sterol	**relative %**
β-sitostanol	41.6
campestanol	6.6
campesterol	1.6
stigmasterol	36.6
other	13.3

Accordingly, the separation of the ester fraction from unsaps and its subsequent hydrolysis has revealed a surprising presence in unsaps of sterols, such as stigmasterol, the presence of which is not normally detected.

Numerous, primarily U.S., patents exist, which disclose the different unsap fractioning technique methods.

Thus, US Patent No. 4,044,031 discloses a method consisting of distilling unsaps in a mixture of solvents including hexane-acetone-methanol, followed by a liquid-liquid extraction process utilizing a hexane-acetone-water mixture, concentrating the extract and then cooling it to obtain a sterol concentrate by crystallization.

US Patent No. 4,420,427 discloses a procedure whereby unsaps undergo hot distillation with methyl ethyl ketone or a mixture of methanol with methyl ethyl ketone. Then, by cooling the mixture, a sterol precipitate is separated, which in turn is separated from the mother liquor by filtration.

A variant of the aforementioned methods is disclosed in U.S. Patent No. 4,265,824, whereby unsaps are dissolved in an organic solvent, followed by the addition of a strong acid,

which causes the preferred formation of a compound with α-sitosterol, and then cooling the mixture, which causes the precipitation of β-sitosterol.

The separation of β-sitosterol and fatty alcohols from tall oil distillation residue or pitch, by high-temperature steam entrainment, between 190 to 280°C, and the vacuum rectification of the vapors of such components has been disclosed in US Patent No. 2,866,739, dated 1958, titled "Recovery of β-sitosterol from tall oil pitch by steam distillation."

Nevertheless, this procedure cannot be applied for the separation of the different components of unsaps, since it involves a series of difficulties, such as the use of high-temperature steam together with considerable thermal decomposition and oxidation of its valuable components.

US Patent No. 4,283,103 discloses a procedure for removing ferric ions from sterol concentrates, in which such concentrates are obtained from plant oils or from tall oil basically through extraction and crystallization techniques. The presence of ferric ions in sterol concentrates, as disclosed, have a negative catalytic effect on their stability. Accordingly, the concentrates undergo complete vacuum evaporation in a falling film column, with the undesirable ferric ions remaining in the residue.

However, short path fractioning of the complex unsaps mixture, with a relatively low content of fatty alcohols, sterols and their esters to produce concentrates of said components is not known in the state of the art.

The unsap fractioning procedure in this invention, on the other hand, allows for the separation of sterols, a fatty alcohol-enriched fraction, from which such alcohols are obtained with ease, and an ester-enriched fraction. The procedure is highly efficient and does not use organic solvents, which, of course, is an additional advantage, considering the increasing environmental restrictions on the use of organic solvents.

Description of the invention

Raw material for the fractioning process

The raw material utilized in the fractioning process is comprised of the unsaponifiable fraction of skimmings deriving from the most part from domestic cellulose companies (CELPAC, ARAUCO, etc.), although it also applies to skimming of any origin. Unsaps can be extracted through procedures known to the state of the art. When the unsaponifiable fraction is extracted using organic solvents, this fraction must first be desolventized prior to its fractioning. Desolventization can be carried out through application of heat either at normal pressure or preferably at reduced pressure.

The raw material for this invention can also be comprised of such unsaps desolventized and enriched through the addition of one or more fractions deriving from the separation process or from any product or sub-product derived from it. Thus, for example, the esters fraction of the unsaps, once separated from such unsaps, can be hydrolyzed and this hydrolyze can be added to the desolventized unsaps deriving from the skimming. Hereinafter the term raw material should be understood as desolventized unsaps. When the raw material consists of unsaps enriched as described, the term enriched raw material will be used.

Description of the process

For purposes of this invention, the complex raw material that is shown in Table I can be conveniently divided into three component groups: one group, known as waxes, due to its physical characteristics, comprised primarily of fatty alcohols, diterpenes, diterpenoids and other unidentified substances; the group of free sterols and stanols, which will be referred to hereinafter simply as sterols; and a group comprised for the most part of esters of fatty alcohols and of sterols, which will be referred to hereinafter as pitch, due to its dark color, caused by the presence in such pitch of compounds from lignin decomposition and oxidized compounds.

The separation of waxes, sterols and pitch from the raw material in this invention is performed by distillation of the raw material into one or more short path distillation columns, also called molecular distillation columns.

To separate the waxes, raw material can be distilled under gentle conditions in a system consisting of a short path distillation column. If so desired, a system with two or more short path distillation columns may also be used. In a multi-column system, the distillate from a first column is used to feed a second column, and the distillate from the second column is used to feed a third column, and so on. The distillate becomes increasingly free of sterols and of esters.

For pitch separation, the raw material can be distilled in a system consisting of a short path distillation column. If so desired, a system of two or more short path distillation columns may be used. In a multi-column system, the residue of the first column is used to feed a second column, and the residue of the second column is used to feel a third column, and so on. The residue becomes increasingly free of sterols and wax.

One of the objectives of this invention is to provide a method for producing a wax essentially free of sterols and pitch. This method includes (1) distillation of raw material in a short path distillation column. For this, the raw material, which is solid at room temperature, is melted at a temperature between 70 to 100°C until it is liquefied, and in this condition it is fed into a short path distillation column at a temperature between 100 to 200°C and at a pressure between 0.01 to 5 mbar to produce a distillate weighing between 35 to 55% in weight per weight of the raw material fed and produce a residue between 45 to 65% in weight per weight of the raw material fed, in which the distillate contains no less than 70% in weight of the free fatty alcohols in relation to the content of such alcohols in the raw material, and (2) collecting the essentially sterol- and pitch-free distillate or wax. To achieve this separation, residence time of the distilland in the column is less than approximately 15 minutes, preferably less than approximately 5 minutes.

Another of the objectives of this invention is to provide a method for producing a wax essentially free of sterols and pitch. This method includes (1) distillation of raw material in a first short path distillation column. For this, the raw material, which is solid at room temperature, is melted at a temperature between 70 to 100°C until it is liquefied, and in this condition it is fed into a short path distillation column at a temperature between 200 to 250°C and at a pressure between 0.01 to 5 mbar to produce a first distillate weighing between 70 to 90% in weight per weight of the raw material fed and produce a first residue between 10 to 25% in weight per weight of the raw material fed, where the distillate contains no less than 70% in weight of the free fatty alcohols in relation to the content of such alcohols in the raw material. To achieve this separation, residence time of the distilland in the first column is less than approximately 15 minutes, preferably less than approximately 5 minutes; (2) collect the first distillate; (3) distill the first distillate in a second short path distillation column at a temperature between 100 to 200°C and at a pressure between 0.01 to 5 mbar to produce a second distillate weighing between 45 to 65% in weight, relative to the weight of the first distillate, and a second residue weighing between 35 to 55% in weight relative to the first distillate. To achieve this separation, residence time of the distilland in the first column is less than approximately 15 minutes, preferably less than approximately 5 minutes; and (4) collect the second distillate or wax essentially free of sterols and of pitch.

Another of the objectives of this invention is to provide a method for producing a sterol concentrate essentially free of wax and pitch. This method includes (1) the distillation of raw material in a first short path distillation column. For this, the raw material, which is solid at room temperature, is melted at a temperature between 70 to 100°C until it is liquefied, and in this condition it is fed into a short path distillation column at a temperature between 200 to 250°C and at a pressure between 0.01 to 5 mbar to produce a first distillate weighing between 70 to 90% in weight per weight of the raw material fed and produce a first residue between 10 to 25% in weight per weight of the raw material fed, where the distillate contains no less than 70% in weight of the free sterols in relation to the content of such free sterols in the raw material. To achieve this separation, residence time of the distilland in the first column is less than

approximately 15 minutes, preferably less than approximately 5 minutes; (2) collect the first distillate; (3) distill the first distillate in a second short path distillation column at a temperature between 100 to 200°C and at a pressure between 0.01 to 5 mbar to produce a second distillate weighing between 45 to 65% in weight, relative to the weight of the first distillate, and a second residue weighing between 35 to 55% in weight relative to the first distillate. To achieve this separation, residence time of the distilland in the second column is less than approximately 15 minutes, preferably less than approximately 5 minutes; and (4) collect the second residue or free sterols essentially free of wax and pitch, in other words, a sterol concentrate.

Another way to achieve the foregoing objectives includes (1) distillation of raw material in a short path distillation column. For this, the raw material, which is solid at room temperature, is melted at a temperature between 70 to 100°C until it is liquefied, and in this condition it is fed into a first short path distillation column at a temperature between 100 to 200°C and at a pressure between 0.01 to 5 mbar to produce a first distillate weighing between 40 to 55% in weight per weight of the raw material fed and produce a first residue between 45 to 60% in weight per weight of the raw material fed, where the first residue contains no less than 70% in weight of the free sterols in relation to the content of such free sterols in the raw material. To achieve this separation, residence time of the distilland in the first column is less than approximately 15 minutes, preferably less than approximately 5 minutes; (2) collect the first residue; (3) distilling the first residue in a second short path distillation column at a temperature between 200 to 250°C and at a pressure between 0.01 to 5 mbar to produce a second distillate weighing between 45 to 65% in weight, relative to the weight of the first distillate, and a second residue weighing between 35 to 55% in weight relative to the first distillate. To achieve this separation, residence time of the distilland in the first column is less than approximately 15 minutes, preferably less than approximately 5 minutes; and (4) collect the second distillate or free sterols essentially free of wax and pitch, in other words, a sterol concentrate.

Another of the objectives of this invention is to provide a method for producing pitch essentially free of free sterols and wax. This method includes (1) the distillation of raw

material in a short path distillation column. For this, the raw material, which is solid at room temperature, is melted at a temperature between 70 to 100°C until it is liquefied, and in this condition it is fed into a short path distillation column at a temperature between 200 to 250°C and at a pressure between 0.01 to 5 mbar to produce a distillate weighing between 75 to 90% in weight per weight of the raw material fed and produce a residue between 10 to 25% in weight per weight of the raw material fed, and (2) to collect the residue or pitch essentially free of sterols and wax. To achieve this separation, residence time of the distilland in the column is less than approximately 15 minutes, preferably less than approximately 5 minutes.

Another of the objectives of this invention is to provide a method for producing pitch essentially free of free sterols and wax. This method includes (1) the distillation of raw material in a short path distillation column. For this, the raw material, which is solid at room temperature, is melted at a temperature between 70 to 100°C until it is liquefied, and in this condition it is fed into a first short path distillation column at a temperature between 100 to 200°C and at a pressure between 0.01 to 5 mbar to produce a first distillate weighing between 40 to 55% in weight per weight of the raw material fed and produce a first residue between 45 to 60% in weight per weight of the raw material fed. To achieve this separation, residence time of the distilland in the column is less than approximately 15 minutes, preferably less than approximately 5 minutes; (2) collect the first residue; (3) distilling the first residue in a second short path distillation column at a temperature between 200 to 250°C and at a pressure between 0.01 to 5 mbar to produce a second distillate weighing between 45 to 65% in weight, relative to the weight of the first distillate, and a second residue weighing between 35 to 55% the weight of the first distillate. To achieve this separation, residence time of the distilland in the column is less than approximately 15 minutes, preferably less than approximately 5 minutes; and (4) collect the second residue or pitch essentially free of wax and free sterols.

Another of the objectives of this invention is to provide a method for producing a sterols and fatty acids compound out of pitch. This method includes (1) hydrolyzing the pitch obtained through the methods described above in an alkaline medium, preferably a

aqueous or alcoholic sodium hydroxide, potassium hydroxide or ammonium hydroxide solution, either pure or in a water solution, in the presence of an organic solvent, preferably an aromatic or aliphatic hydrocarbon, at a temperature between 100 to 300°C and for a sufficient period of time to produce the hydrolysis of the pitch esters; (2) cooling the mixture; (3) separating the organic phase; (4) washing the separated organic phase in an aqueous ethanol or methanol solution; (5) desolventizing the washed organic phase to obtain a compound of free sterols and fatty alcohols. If so desired, this compound may be added to the raw material to obtain enriched raw material, or it can be added to a sterol concentrate. Alternately, hydrolysis can be performed without the presence of an organic solvent. In that case, the solvent is added once the pitch is hydrolyzed, extracting the alcohols and sterols from the hydrolysate, and then proceeding as described above.

Another of the objectives of this invention is to provide a method for the production of a sterol compound with a sterol content of no less than 90% in weight, relative to the weight of that compound. This method includes (1) mixing the sterol fraction deriving from a second short path distillation column with acetone, methyl ethyl ketone, methanol or ethanol, or a mixture of these; (2) stirring at room temperature or refluxing the mixture; (3) cooling the mixture to a temperature of approximately –20 to 20°C; (4) separating the crystals produced during the cooling stage; and (5) desolventizing those crystals.

The technique described is the one customarily used for crystallizing sterols from raw materials with a sterol content of less than 50% in weight, although it is also applicable to raw materials with higher sterol content.

For the sterol concentrates obtained by the methods in this invention, another form exists for obtaining almost pure sterols, which includes (1) mixing the concentrate with acetone or another solvent; (2) cold stirring; (3) separating the solids from the mother liquor, for example, by filtration; and (4) desolventizing the solids. In other words, it involves a simple cold washing of the concentrate with a solvent. This process is only possible for the products in this invention, in which sterol content is so high that instead of recrystallizing them, it is enough to wash them.

This is another well-known additional advantage of this invention compared to the traditional total dissolution and recrystallization methods.

Another of the objectives of this invention is to provide a method for producing a fatty alcohol concentrate between 20 to 26 carbons with a fatty alcohol content of no less than 75% in weight relative to the weight of the alcohol concentrate. This procedure includes (1) mixing the wax deriving from a first or second column with a solvent, preferably an aliphatic or aromatic hydrocarbon; (2) refluxing the mixture; (3) cooling the mixture; (4) separating the crystals produced during the cooling stage; and (5) desolventizing the crystals.

Another of the objectives of this invention is to provide a method for producing a mixture of wax and free sterols, essentially free of pitch. This method includes (1) the distillation of raw material in a short path distillation column. For this, the raw material, which is solid at room temperature, is melted at between 70 to 100°C until it is liquefied, and in this condition it is fed into a short path distillation column at a temperature between 200 to 250°C and at a pressure between 0.01 to 5 mbar to produce a distillate weighing between 75 to 90% in weight per weight of the raw material fed and produce a residue weighing between 10 to 25% in weight per weight of the raw material fed; and (2) collecting the essentially pitch-free distillate. To achieve this separation, residence time of the distilland in the column is less than approximately 15 minutes, preferably less than approximately 5 minutes.

Another of the objectives of this invention is to provide a method for the production of a sterol concentrate essentially free of wax and pitch. This method includes (1) mixing the first distillate of a first short path distillation column with acetone, methyl ethyl ketone, methanol or ethanol or a mixture of these; (2) refluxing this mixture; (3) cooling the mixture to a temperature approximately between –20 to 20°C; (4) separating the crystals produced during the cooling stage; and (5) desolventizing those crystals.

Another of the objectives of this invention is to provide a method for the production of a wax concentrate essentially free of sterols and pitch. This method includes (1) mixing the first distillate of a first short path distillation column with acetone, methyl ethyl ketone, methanol or ethanol or a mixture of these; (2) refluxing the mixture; (3) cooling the mixture to a temperature approximately between –20 to 20°C; (4) separating the crystals produced during the cooling stage; and (5) desolventizing the mother liquor to recover a wax concentrate.

Another of the objectives of this invention is to provide a method for the production of a fatty alcohol concentrate essentially free of sterols and pitch. This method includes (1) mixing the first distillate of a first short path distillation column with acetone, methyl ethyl ketone, methanol or ethanol or a mixture of these; (2) refluxing this mixture; (3) cooling the mixture to a temperature of approximately between –20 to 20°C; (4) separating the crystals produced during the cooling stage; (5) desolventizing the mother liquor; (6) dissolving the residual solid from stage (5) desolventization with hexane, heptane, toluene, xylene or a mixture of these; (7) refluxing the mixture; (8) cooling the mixture to a temperature approximately between –20 to 20°C; (9) separating the crystals produced during the cooling stage; and (10) desolventizing those crystals.

Another of the objectives of this invention is to provide a method for the production of a sterol concentrate essentially free of wax and pitch. This method includes (1) mixing the first residue of a first short path distillation column with acetone, methyl ethyl ketone, methanol or ethanol or a mixture of these; (2) stirring at room temperature or refluxing the mixture; (3) cooling the mixture to a temperature approximately between –20 to 20°C; (4) separating the crystals produced during the cooling stage; and (5) desolventizing those crystals.

Another of the objectives of this invention is to provide a method for the production of pitch essentially free of sterols and waxes. This method includes (1) mixing the first residue of a first short path distillation column with acetone, methyl ethyl ketone, methanol or ethanol or a mixture of these; (2) refluxing this mixture; (3) cooling the mixture to a temperature

approximately between –20 to 20°C; (4) separating the crystals produced during the cooling stage; and (5) desolventizing the mother liquor to obtain a pitch concentrate.

The pitch obtained through the methods in this invention can conveniently be purified or its color lightened to obtain an ester concentrate suitable for use in food.

For this, the dark-colored pitch can be distilled in a short path distillation column, with the evaporator at the same or a higher temperature than 250°C and with the condenser at a temperature between 150°C to 200°C and at a pressure between 0.01 to 5 mbar. Surprisingly, it has been discovered that the distillate under those conditions is clear or of a slight amber color, while the dark, oxidized, or decomposed material stays in the column residue.

Another way to purify or lighten the color of pitch to make it suitable for human use consists of the adsorption of the dark impurities with active carbon or another adsorbent. The manner in which such color lightening is carried out will be described in the examples.

Of course, the color of pitch can also be lightened prior to its hydrolysis for the production of free sterols or stanols or fatty alcohols, if so desired.

The phrase "essentially free" in this invention is to be interpreted as follows:

Wax essentially free of pitch: Fraction of raw material with a fatty alcohol and sterol ester content of less than 20% in weight of esters relative to the content of such esters in the raw material and a fatty alcohol content of no less than 70% in weight of such alcohols relative to the content of such alcohols in the raw material.

Wax essentially free of free sterols: Fraction of the raw material with a free sterol content less than 20% in weight of free sterols relative to the sterol content of the raw material and a fatty alcohol content of no less than 70% in weight of such alcohols relative to the content of such

alcohols in the raw material.

Sterols essentially free of pitch: Fraction of the raw material with a fatty alcohol and sterol ester content less than 20% in weight of esters relative to the content of such esters in the raw material and a free sterol and stanol content of no less than 70% in weight of such free sterols and stanols relative to the content of such free sterols in the raw material.

Sterols essentially free of wax: Fraction of the raw material with a free fatty alcohol content less than 20% in weight of such alcohols relative to the content of such alcohols in the raw material and a free sterol and stanol content of no less than 70% in weight of such free sterols and stanols relative to the content of such free sterols in the raw material.

Pitch essentially free of wax: Fraction of the raw material with a free fatty alcohol content less than 20% of the content of such free alcohols relative to the raw material and an alcohol and sterol ester content of no less than 70% in weight of such alcohols relative to the content of such alcohols in the raw material.

Pitch essentially free of sterols: Fraction of the raw material with a free sterol and stanol content less than 20% of the content of such frees sterols and stanols relative to the content of such free sterols and stanols in the raw material and a content of fatty alcohol and sterol esters of no less than 70% in weight of such alcohols relative to the content of the alcohols in the raw material.

Description of the drawings

For its purposes, this invention uses what is known as a short path distillation column or a molecular distillation column, which under the operating conditions in this invention efficiently separates the complex mixture of neutral compounds from the raw material into wax, free sterol concentrate, and pitch. In a conventional vacuum distillation column, the distance between the

evaporation surface and the condensation surface is much greater than the mean free path of the molecules at operating pressure, and the device generally consists of a reboiler, a fractioning column, and a vacuum-operating condenser. In a molecular distillation column, the path for the steam to reach the condenser is not obstructed because the condenser is separated from the evaporator by a distance that is smaller than the mean free path of the molecules that are being distilled. Usually, in a molecular distiller, the mean free path of the molecules is a few centimeters. Nevertheless, in order to achieve higher distillation rates, the distance between the evaporation surface and the condensation surface is slightly greater than the distance of the mean free path. Short path distillation columns, in which the evaporation surface and the condensation surface are close to each other, are adequate for the objectives of this invention. Such surfaces are considered to be close when the distance between those surfaces is less than approximately 50 centimeters, preferably between approximately 3 and 50 centimeters. Such short path distillation columns operate in many aspects in a manner similar to a molecular distiller.

Falling film short path distillation columns with or without scrapers, centrifugal short path distillation columns, multistage short path distillation columns and others are adequate types of columns for the purposes of this invention.

Figure 1 shows a short path distillation column with scrapers and all of the auxiliary equipment used in this invention, which is available from UIC GmbH and its U.S. subsidiary UIC Inc. Of course, other short path distillation columns or evaporators can be used. This invention can now be explained with reference to Figures 1, 2, and 3.

In reference to Figure 1, short path distillation column **1** has an evaporation surface **2** located near to a hollow internal condenser **3**, inside which a heating fluid is made to flow, which enters through inlet **17** and leaves through outlet **18**. The source of this heat transference fluid is not shown. Raw material **5** is fed from the top to a double wall graduated feeder **6**

equipped with an inlet **32** and an outlet **33** for a heat transference fluid, which maintains the raw material in liquid state. The heating fluid source is not shown. Raw material 5 flows downward through the surface of evaporator **2**, while a scraper distributor **7** spreads the raw material **5** on surface **2**. A motor **8** equipped with a speed regulator **9** placed near the top of evaporator 1 on flange **10** causes the axis **11** and scraper distributor **7** to rotate. The combined effect of gravity and the scraper distributor **7** allows for the falling movement of a thin and uniform film over the entire surface of evaporator **2**. Heat is applied to the thin film on the evaporator surface by making a heat transference fluid circulate through jacket **12.** The heat transference fluid enters through inlet **13** and leaves through outlet **14**. The source of the heat transference fluid is not shown. The temperature of the heat transference fluid in jacket **12** of column **1** is at least 50°C lower than the temperature of the heat transference fluid in inner condenser **3** of column **1**. An adequate heat transference fluid can be water, pressurized water, steam, ethylene glycol, oil, or similar fluids.

Space **15** between the surface of evaporator **2** and the inner condenser **3** is evacuated through vacuum line **16** connected to a double wall cold trap **21**, whose interior **21** contains a cooling medium, which may be liquid air or dry ice with isopropanol, for example. The vacuum and heat combination allows volatile components to escape from the thin film, to travel through space **15**, and to condense on inner condenser **3**. More volatile components are retained in the cold trap. The distilland, which is not shown, flows down in the form of a thin film on evaporator surface **2** and is received in flask **19**. The distillate flows down through the outer surface of inner condenser **3** and is received in flask **20**. As the thin film flows downward, it is enriched with pitch or with pitch plus sterols. The vacuum in space **15** is produced by a rotary vane vacuum pump **23** equipped with an exhaust gas filter and connected to outlet **4** of cold trap **21** through a diffusion pump **25**. A pressure sensor **26** sends an electric signal to a pressure meter **28**, which indicates the pressure in space **15**. A micrometric valve **27** located at the entry of diffusion pump **25** allows for regulating pressure by the controlled entry of air through inlet **34**. Column **1** and its accessories

are fixed to a metallic bracket **30**, which rests on a base **31**. An electric panel **29** contains the connections for the pressure sensor **26**, motor **8,** diffusion pump **25**, vacuum rotary pump **23** and the thermostats for the heat transference fluids, which are not shown.

Using a distillation system containing only one short path distillation column as shown in Figure 1, the distilled fraction generally consists of wax or wax with free sterols. When the distilled fraction collected in flask **20** consists of wax with free sterols, this fraction can be fed into another short path distillation column (see Figure 2) to produce a distilled fraction essentially free of free sterols and a residue essentially free of wax.

When the fraction distilled in the first column collected in flask **20** consists essentially of wax, the residue collected in flask **19** may be fed into a second short path distillation column (see Figure 3) to produce a distilled fraction essentially free of pitch and a residue essentially free of free sterols.

Generally, a short path distillation column system is preferred. However, in some cases it is preferable to use a series of two or more short path distillation columns. The use of multiple short path distillation columns is illustrated in Figures 2 and 3.

In Figure 2, column **100** and **200** both are schematically illustrated short path distillation columns, and they may be similar to the one in Figure 1 or they may be of another type of short path evaporation column design. The raw material is fed through line **101** to dosing accumulator reservoir **102** of column **100**. The raw material is fed through line **103** to the top of column **100** in such a manner that it flows in the form of a film over surface **104** of column **100.** A scraper distributor system (not shown) can be used, as shown in Figure 1, to ensure uniform distribution over the column surface. Column **100** has a jacket **105** to transfer heat to column surface **104**, by means of a heat transference fluid that is fed to jacket **105** through line **106** and is evacuated through line **107**. In addition, the column has an inner condenser **108** close to surface **104**

separated by space **109**. Through vacuum pump **111**, a vacuum is applied to space **109** through line **110**. The distillate flows through condenser **108** to leave column **100** through line **113**. In turn, the distilland or distillation bottom flows over surface **104** to leave the column through line **112**.

The distillate or distillation top from column **100** is conducted through line **113** to dosing accumulator reservoir **202** of column **200**. The distilland from column **100** is fed to the top of column **200** through line **203** so that it flows in the form of a film over surface **204** of column **200**. A scraper distributor system (not shown) can be used as shown in Figure 1 to ensure uniform distribution over the column surface. Column **200** has a jacket **205** to transfer heat to surface **204** of the column, by means of a heat transference fluid that is fed to jacket **205** through line **206** and is evacuated through line **207**. In addition, the column has an inner condenser **208** close to surface **204** separated by space **209**. Through vacuum pump **211**, a vacuum is applied to space **209** through line **210**. The distillate flows through condenser **208** to leave column **200** through line **213**. In turn, the distilland or distillation bottom flows over surface **204** to leave the column through line **212**.

In Figure 3, column **300** and **400** both are schematically illustrated short path distillation columns, and they may be similar to the one in Figure 1 or they may be of another type of short path evaporation column design. The raw material is fed through line **301** to dosing accumulator reservoir **302** of column **300**. Raw material is fed through line **303** to the top of column **300** in such a manner that it flows in the form of a film over surface **304** of column **300**. A scraper distributor system (not shown) may be used as shown in Figure 1 to ensure uniform distribution over the column surface. Column **300** has a jacket **305** to transfer heat to column surface **304**, by means of a heat transference fluid that is fed to jacket **305** through line **306** and is evacuated through line **307**. In addition, the column has an inner condenser **308** close to surface **304** separated by space **309**. Through vacuum pump **311**, a vacuum is applied to space **309** through

line **310**. The distillate flows through condenser **308** to leave column **300** through line **312**. In turn, the distilland or distillation bottom flows over surface **304** to leave the column through line **313**.

The distilland or distillation bottom from column **300** is conducted through line **313** to dosing accumulator reservoir **402** of column **400**. The distilland from column **300** is fed to the top of column **400** through line **403** so that it flows in the form of a film over surface **404** of column **400**. A scraper distributor system (not shown) may be used as shown in Figure 1 to ensure uniform distribution over the column surface. Column **400** has a jacket **405** to transfer heat to surface **404** of the column, by means of a heat transference fluid that is fed to jacket **405** through line **406** and is evacuated through line **407**. In addition, the column has an inner condenser **408** close to surface **404** separated by space **409**. Through vacuum pump **411**, a vacuum is applied to space **409** through line **410**. The distillate flows through condenser **408** to leave column **400** through line **213.** In turn, the distilland or distillation bottom flows over surface **404** to leave column **400** through line **412**.

The invention is illustrated in greater detail though not limited by the following examples. The analytical techniques utilized are described after the examples that follow.

In the examples described below, a raw material containing approximately 52% wax, 33% free sterols, and 15% esters or pitch was utilized.

Example 1

Wax production

The graduated feeder of the short path distillation column shown in Figure 1 was loaded with 94 grams of melted raw material. Temperature in the feeder was kept at 80°C by the circulation of water in the jacket. Temperature in the column jacket was kept at 150°C by the circulation of a mineral oil at that temperature. Condenser temperature was 80°C. Once the pressure in the column reached a value of 0.1 mbar (absolute pressure), it began to be fed with the scraper distributor rotating at a speed of approximately 200 rpm. Feed rate was of approximately 1 ml per minute. Once the operation was finished, a distillate was collected that weighed 40.4 grams, i.e. 43% in weight of the raw material fed. The mass collected in the cold trap was 2% in weight of the feed.

The composition of the distillate was of 95% wax and 3.8% sterols. In the wax fraction, approximately 94% of docosanol from the feed and 91% of tetracosanol from the feed is to be found.

Example 2

Pitch production

The short path distillation column feeder was loaded with 104 grams of raw material at 80°C. Temperature in the column evaporator was 230°C and temperature in the condenser was 195°C. Operating pressure was 0.1 mbar and the feed rate was approximately 1 ml per minute with the scraper distributor rotating at a speed of approximately 200 rpm. At the end of the operation, the mass collected in the cold trap was 6.1% in weight of the feed mass, while the distillate mass was 76.1% in weight of the mass of raw material fed. Pitch or residue was 17.8% in weight of the mass of raw material fed and had approximately 81% sterol and fatty alcohol esters, 18% sterols and 1% wax.

Example 3

Wax and free sterol production

The short path distillation column feeder was loaded with 50 grams taken from the distillate from Example 2. Feeder temperature was kept at 95°C. Temperature in the column evaporator was 150°C and the temperature in the condenser was 80°C. Operating pressure was 0.1 mbar and the feed rate was approximately 1 ml per minute with the scraper distributor rotating at a speed of approximately 200 rpm. Distillate collected was 50.61% in weight of the feed, with a composition of 90% wax and 10% sterols. Fatty alcohols in this flow correspond approximately to 70% of the total fatty alcohols fed. Approximately 87% of the sterols fed are to be found in the distilland or distillation bottom. No mass was collected in the cold trap.

Example 4

Sterol and pitch production

The short path distillation column feeder is loaded with 43 grams taken from the residue from Example 1 at a temperature of 100°C, and they are fed into the column evaporator at a rate of 1 ml per minute. Evaporator temperature was 230°C, the condenser temperature was 145°C, and pressure in the column was kept at 0.1 mbar with the scraper distributor rotating at a speed of approximately 200 rpm. At the end of the operation, collected distillate weighed 29 grams, representing 67.4% in weight of the mass fed, and the residue was 14 grams, representing 32.6% in weight of the mass fed. There was no distillate in the cold trap. The top flow has approximately 92% of the sterols fed, and the bottom flow, 90% of the sterol and fatty alcohol esters.

Example 5

Pitch hydrolysis

This example uses 100 grams of pitch, produced as described in Example 4, with a free sterol content of approximately 5.2% in weight, mixed with 300 grams of a 15% methanolic KOH solution with 300 grams of toluene and loaded into a Parr model 4522 pressure reactor, where they were left to react while stirring at a temperature of 252°C and at pressure of 53 bar for three hours. Once the reactor content cooled, the mixture was emptied into a decanting funnel, recovering the upper organic phase. This phase was mixed with 50 ml of an aqueous ethanolic solution at a 1:1 volume, and was stirred vigorously for several minutes, and poured immediately afterward into a decanting funnel. This operation was repeated until the aqueous solution resulting from the washing of the organic phase had a neutral pH. The organic phase separated was desolventized. The solids recovered weighed 92.7 grams and their composition as a percentage in weight of the mass recovered was: free sterols 43.2%; fatty alcohols 19%; and fatty acids 36%.

Example 6

Obtaining fatty alcohol concentrate

We took 55 grams of wax obtained as described in Example 1, which were mixed with 250 ml of hexane and heated and refluxed for 15 minutes, after which they were allowed to cool at a rate of approximately 1°C per minute until they reached a temperature of 5°C. The crystallized mixture was filtered in a Kitasato vacuum flask, in a Büchner filter using Whatman No. 5 filter paper. The crystals were desolventized in a vacuum oven at 1 mbar and at 100°C for 6 hours. The crystals thus obtained have a fatty alcohol content of 90% with the purity indicated in Table 3:

Table 3

Relative purity of fatty alcohols obtained from the wax

compound	relative %
eicosanol	5.9
docosanol	52.0
tetracosanol	30.0
hexacosanol	1.2
sterols	8.0

Example 7

Production of a free sterol compound 1

We took 25 grams of sterol concentrate produced as described in Example 3, mixed them with 96 ml of acetone, and refluxed them for 15 minutes, after which they were left to cool at a cooling rate of approximately 1°C per minute until they reached a temperature of 5°C. The crystallized mixture was filtered in a Kitasato vacuum flask, in a Büchner filter using Whatman No. 5 filter paper. The crystals were desolventized in a vacuum oven at 1 mbar and at 100°C for 6 hours. The crystals thus obtained have a sterol purity of 92.7%.

Example 8

Production of a free sterol compound 2

We took 15 grams of sterol concentrate produced as described in Example 4, mixed them with 40 ml of acetone at a temperature of –5°C in a 100 ml Erlenmeyer flask. The mixture was stirred for 5 minutes using a magnetic stirrer. Next the mixture was filtered in a Kitasato vacuum flask, in a Büchner filter using Whatman No. 5 filter paper. The solids were desolventized in a vacuum oven at 1 mbar and at 100°C for 6 hours. The solids thus obtained have a sterol purity of 87%.

Example 9

Purification of wax and sterol concentrate

We took 30 grams of the top flow generated in Example 2. They were mixed with 60 g of methanol, refluxed for 15 minutes, after which they were allowed to cool at a cooling rate of approximately 1°C per minute until they reached a temperature of 5°C. The crystallized mixture was filtered in a Kitasato vacuum flask, in a Büchner filter using Whatman No. 5 paper filter. The crystals thus obtained had a sterol purity of 77%.

Example 10

Purification of the wax filtrate

The methanolic mother liquor resulting from the filtration of Example 9 was taken, desolventized and cooled in a vacuum desiccator. The resulting mass was dissolved in a solid: hexane ratio of 1 : 2 and refluxed for 15 minutes, after which it was allowed to cool at a cooling rate of approximately 1°C per minute until they reached a temperature of 5°C. The mixture crystallized was filtered in a Kitasato vacuum flask in a Büchner filter using Whatman No. 5 filter paper. The crystals thus obtained had a purity of 47% docosanol and 21% tetracosanol.

Example 11

Purification of sterol and pitch concentrate

We took 45 grams of the bottom flow generated in Example 1. They were mixed with 150 ml of methyl ethyl ketone and refluxed for 15 minutes, after which they were allowed to cool at a cooling rate of approximately 1°C per minute until they reached a temperature of 0°C. The crystallized mixture was filtered in a Kitasato vacuum flask, in a Büchner filter using Whatman

No. 5 paper filter. The crystals thus obtained had a sterol purity of 81%.

Example 12

Hydrolysis of the pitch filtrate

The mother liquor resulting from the filtration of Example 11 was taken, desolventized and cooled in a vacuum desiccator. The resulting mass has 52% esters and 45% sterols. We used 10 grams of the mass and dissolved them with 40 g of a 15% methanolic KOH solution and with 40 grams of toluene, then loaded it into a Parr model 4522 pressure reactor, where they were left to react under stirring at a temperature of 254°C and at a pressure of 59 bar for three hours. Once the reactor content cooled, the mixture was emptied into a decanting funnel, recovering the upper organic phase. This phase was mixed with 25 ml of an aqueous ethanolic solution in a 1:1 volume and stirred vigorously for several minutes, then poured immediately afterward into a decanting funnel. This operation was repeated until the aqueous solution resulting from the washing of the organic phase had a neutral pH. The organic phase separated was desolventized. The solids recovered weighed 9.6 grams, and the analysis of their composition yielded 67% free sterols and 10% fatty alcohols.

Example 13

Purification of Pitch 1

We took 25 g of the pitch concentrate obtained in Trial 2 and loaded them into the short path distillation column feeder, heated to 200°C with mineral oil. The temperature of the column evaporator was 250°C and the condenser temperature was 200°C. The operating pressure was 0.1 mbar and the feed rate was approximately 1 ml per minute with the scraper distributor rotating at a speed of approximately 200 rpm. At the end of the operation, the mass collected in the distillate was 24 grams, corresponding to 97% of the mass fed. The mass thus obtained has a light

amber coloring, notably less intense than the dark-colored mass fed.

Example 14

Purification of Pitch 2

We took 35 g of the pitch concentrate obtained in Trial 4 and they were dissolved to 5% with chloroform at room temperature, obtaining a black solution. The solution was separated through a glass column with a 15 mm i.d. and 30 cm long porous frit loaded halfway with aluminum oxide soaked in chloroform, at a rate of 10 ml / min at room temperature. The resulting orangey yellow colored solution was desolventized in a Büchi brand model R-124V rotavapor at 10 mbar. The resulting mass is of a crystalline amber color.

Description of the analytical technique: Chromatographic Analysis

The identification and determination of the components of the unsap and unsap fractions obtained through the patent description was performed through capillary column gas chromatography. The chromatographic methodology employed is the result of an extensive study of the most appropriate conditions and techniques to determine the components present in the unsap and unsap fractions.

(a) Chromatographic operating parameters

Hewlett Packard model HP 5890 series 2 chromatograph
capillary column HP-5, 30 m long, 0.32 mm di, 0.25 μm film

furnace temperature:	300°C (isotherm)
injector temperature:	320°C
detector temperature:	320°C
carrier (He) flow:	0.92 ml/min
split:	60:1
programmed duration:	15 min
injection:	0.5 μl

(b) Sample preparation

- Weigh approximately 100 mg of sample with an accuracy of 1 mg in a 25 ml graduated flask
- Dissolve completely with tetrahydrofurane (THF) and level off
- Add exactly 500 µl of the solution prepared beforehand in a silanization tube
- At the same time, weigh approximately 50 mg of 5β-colestan-3α-ol in a 100 ml graduated flask with an accuracy of 0.1 mgr
- Dissolve completely in n-propanol and level off
- Add exactly 500 µl of the 5β-colestan-3α-ol solution to the silanization tube
- Dry under nitrogen atmosphere with low heating
- Add 300 µl of Bis (trimethylsilyl) trifluoroacetamide (BSTFA)
- Add 300 µl of pyridine
- Maintain the solution at 70°C for 10 minutes
- Dry under inert atmosphere
- Dissolve with 500 µl of THF

Note: All the reagents must be analytic grade.

(c) Calculations

- Record the area of the compound of interest
- Record the area of 5β-colestan-3α-ol
- Calculate the weight percentage of the compound of interest through the following formula:

$$\%X = \frac{A_x \cdot M_p}{A_p \cdot M_m} \cdot 100$$

Where, X: percentage in weight of the compound of interest

A_x: chromatographic area of the compound of interest

M_p: pattern added mass (5β-colestan-3α-ol)

A_p: pattern chromatographic area (5.beta.-colestan-3 .alpha.-ol)

M_m: sample added mass

[page 30-31 are missing]

CLAIMS

1. A method for separating components from a raw material containing neutral black-liquor soap compounds CHARACTERIZED because it includes:

(a) feeding the raw material into a short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 100°C to 200°C and with the condenser of that column at a temperature between 60°C to 100°C to form a distillate weighing between 35% to 55% in weight per weight of the raw material fed.

(b) collecting the distillate as wax essentially free of sterols and pitch

(c) a short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters

(d) a residence time in the column for the feed material of less than 15 minutes.

2. A method for separating components from a raw material containing neutral black-liquor soap compounds CHARACTERIZED because it includes:

(a) feeding the raw material to a first short path distillation column at a pressure between of 0.01 to 5 mbar, with the column evaporator at a temperature between 200°C to 250°C and with the condenser of that column at a temperature between 100°C to 180°C to form a distillate weighing between 70% to 90% in weight per weight of the raw material fed.

(b) collecting the first distillate

(c) feeding the first distillate collected in (b) or a part of that first distillate to a second short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 100°C to 200°C and with the condenser of that column at a temperature between 50°C to 120°C to form a second distillate, weighing

between 45% to 65% in weight per weight of the second column feed.

(d) collecting the second distillate as wax essentially free of sterols and pitch

(e) a first short-path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters and a second short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters

(f) a residence time in the first column for the feed material of less than 15 minutes and a residence time in the second column for the feed material of less than 15 minutes.

3. A method for producing a fatty alcohol concentrate of between 20 to 26 carbons approximately according to claim 1 or 2 CHARACTERIZED because it includes:

(a) mixing the distillate collected in stage (b) or a part of that distillate with an organic solvent or mixing the second distillate collected in stage (d) or a part of that distillate with an organic solvent

(b) heating or refluxing the stage (a) mixture

(c) cooling the stage (b) mixture to a temperature of –20 to 20°C or less

(d) collecting the solids produce in stage (c)

(e) desolventizing the solids produced in stage (d)

(f) collecting the stage (e) solids

4. The method according to claim 3 CHARACTERIZED because the stage (a) solvent is hexane, heptane or any aliphatic hydrocarbon with 6 to 10 carbon atoms, benzene, xylene, or toluene or a mixture of any of two or more such solvents.

5. The method according to claim 2 or 3 CHARACTERIZED because stage (c) solids contain no less than 70% in weight of docosanol or tetracosanol.

6. A method for separating components of a raw material containing neutral black-liquor soap compounds CHACTERIZED because it includes:

(a) feeding the raw material to a first short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 200°C to 250°C and with the condenser of that column at a temperature between 100°C to 180°C to form a first distillate weighing between 70% to 90% in weight per weight of the raw material fed.

(b) collecting the first distillate

(c) feeding the first distillate collected in stage (b) or a part of that first distillate to a second short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 100°C to 200°C and with the condenser of that column at a temperature between 60°C to 120°C to form a second distillate weighing between 35% to 55% in weight per weight of the second column feed.

(d) collecting the second distillate as sterols essentially free of wax and pitch

(e) a first short-path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters and a second short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters

(f) a residence time in the first column for the feed material of less than 15 minutes and a residence time in the second column for the feed material of less than 15 minutes

7. A method for separating components of a raw material containing neutral black-liquor soap compounds CHARACTERIZED because it includes:

(a) feeding the raw material to a first short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 100°C to 200°C and with the condenser of that column at a temperature between 60°C to 100°C to form a first residue weighing between 45% to 55% in weight per weight of the raw material fed.

(b) collecting the first residue

(c) feeding the first residue collected in stage (b) or a part of that first residue to a second short path distillation column at a pressure between 0.01 to 5 mbar and with the column evaporator at a temperature between 200°C to 250°C, to form a second distillate weighing between 45% to 65% in weight per weight of the second column feed.

(d) collecting the second distillate as sterols essentially free of wax and pitch

(e) a first short-path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters and a second short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters.

(f) a residence time in the first column for the feed material of less than 15 minutes and a residence time in the second column for the feed material of less than 15 minutes.

6. The method according to claim 6 or 7 for producing a sterol compound CHARACTERIZED because it includes:

(a) mixing the second residue collected in stage (d) or a part of that second residue with an organic solvent or mixing the second distillate collected in stage (d) or a part of that second distillate with an organic solvent

(b) heating or refluxing the stage (a) mixture

(c) cooling the stage (b) mixture to a temperature of –20 to 20°C

(d) separating the solids produced in stage (c)

(e) desolventizing the stage (d) solids

(f) collecting the stage (e) solids

9. The method according to claim 8 CHARACTERIZED because the stage (a) solvent is acetone, methyl ethyl ketone or any dialkyl ketone containing between 3 to 10 carbon atoms, methanol or ethanol or any aliphatic alcohol with 1 to 6 carbon atoms or a mixture of any of two or more of such solvents.

10. The method according to claim 8 or 9 CHARACTERIZED because the desolventized stage (f) solids contain at least 90% in weight of free sterols or stanols.

11. The method according to claim 6 or 7 for producing a sterol compound CHARACTERIZED because it includes:

(a) mixing a second residue collected in stage (d) or a part of that second residue with an organic solvent or mixing the second distillate collected in stage (d) or a part of that second distillate with an organic solvent

(b) stirring the stage (a) mixture at room temperature or at a temperature lower than room temperature

(c) separating the solid and liquid phase of the stage (b) mixture

(d) desolventizing the solid phase of stage (c)

(e) collecting the stage (d) solids

12. The method according to claim 11 CHARACTERIZED because the stage (a) solvent is acetone, methyl ethyl ketone or any dialkyl ketone containing between 3 to 10 carbon atoms, methanol or ethanol or any aliphatic alcohol with 1 to 6 carbon atoms or a mixture of any of two or more of such solvents.

13. The method according to claim 11 or 12 CHARACTERIZED because the desolventized stage (e) crystals contain at least 90% in weight of free sterols or stanols.

14. A method for separating components of a raw material containing neutral black-liquor soap compounds CHARACTERIZED because it includes:

(a) feeding the raw material to a short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 200°C to 250°C and with the condenser of that column at a temperature between 100°C to 180°C to form a residue weighing between 10% to 320% in weight per weight of the raw material fed.

(b) collecting the residue as pitch essentially free of sterols and wax

(c) a short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters

(d) a residence time in the column for the feed material that is less than 15 minutes.

15. A method for separating components of a raw material containing neutral black-liquor soap compounds CHARACTERIZED because it includes:

(a) feeding the raw material to a first short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 100°C to 200°C and with the condenser of that column at a temperature between 60°C to 100°C to form a first residue weighing between 45% to 65% in weight per weight of the raw material fed.

(b) collecting the first residue

(c) feeding the first residue collected in stage (b) or a part of that first residue to a second short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 200°C to 250°C and with the condenser of that column at a temperature between 100°C to 200°C to form a second residue weighing between 25% to 35% in weight per weight of the raw material fed.

(d) collecting the second residue as pitch essentially free of wax and sterols.

(e) a first short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters and a second short path distillation column with an evaporation and a condensation surface separated by a distance no greater than 50 centimeters.

(f) a residence time in the first column for the feed material of less than 15 minutes and a residence time in the second column for the feed material of less than 15 minutes.

16. The method according to claim 14 or 15 for producing a compound of sterol or stanol or fatty alcohol esters CHARACTERIZED because it includes:

(a) feeding the residue collected in stage (b) or a part of that reside or feeding the second residue of stage (d) or a part of that residue to a short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature of 250°C or greater and with the condenser of that column at a temperature between 120°C to 200°C to form a distillate with a weight greater than 90% in weight per weight of the raw material fed.

(b) collecting the distillate as a sterol or stanol ester compound.

(d) a short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters

(e) a residence time in the column for the feed material of less than 15 minutes

17. The method according to claim 14, 15 or 38 for producing a compound of sterol or stanol or fatty alcohol esters CHARACTERIZED because it includes:

(a) dissolving the residue collected in stage (b) or a part of that residue in an organic solvent or dissolving the second residue of stage (d) or a part of that reside in an organic solvent or dissolving the distillate of stage (b) or a part of that distillate in an organic solvent or dissolving the solids of stage (f) or a part of those solids in an organic solvent

(b) putting the stage (a) solution in contact with an adsorbent

(c) separating the solution and the stage (b) adsorbent

(d) desolventizing the stage (c) solution

(e) collecting the stage (d) desolventized solids

18. The method according to claim 17 CHARACTERIZED because the stage (a) organic solvent is an aromatic hydrocarbon or a chlorinated hydrocarbon.

19. The method according to claim 18 CHARACTERIZED because the stage (a) organic solvent [is] chloroform or carbon tetrachloride.

20. The method according to claim 18, 19 or 20 CHARACTERIZED because the stage (b) adsorbent is active carbon or alumina or silicates or diatomaceous earth.

21. The method according to claim 16, 17, 18, 19 or 20 CHARACTERIZED because the compound of sterol or stanol or fatty alcohol esters contains no less than 90% in weight of such esters.

22. A method for producing a compound of free sterols, stanols or fatty alcohols according to claims 14, 15, 16, 17, 18, 19, 20, 21 or 38 CHARACTERIZED because it includes:

(a) mixing the residue collected in stage (b) or a part of that residue or mixing the second residue of stage (d) or a part of that second residue or mixing the solids of stage (e) or a part of such solids or mixing a compound of sterol or stanol or fatty alcohol esters or mixing the solids of stage (f) or a part of such solids with an aqueous or alcoholic solution of sodium or potassium or ammonium hydroxide or pure ammonium and an organic solvent.

(b) heating the stage (a) mixture to a temperature of 100°C to 300°C for a sufficient time

(c) cooling the stage (b) mixture

(d) separating the organic phase of the stage (c) mixture

(e) mixing the organic phase of stage (d) with water

(f) evaporating the organic phase and the water of stage (e)

(g) desolventizing the organic phase separated from stage (f).

(h) collecting solids produced in stage (g)

23. The method according to claim 22 CHARACTERIZED because the stage (a) solvent is an aromatic or aliphatic hydrocarbon.

24. The method according to claim 23 CHARACTERIZED because the solvent is toluene or xylene or hexane.

25. The method according to claim 22, 23, or 24 CHARACTERIZED because the stage (h) solid compound contains at least 50% in weight of free sterols, stanols or fatty alcohols.

26. A method for separating components of a raw material containing neutral black-liquor soap compounds CHARACTERIZED because it includes:

(a) feeding the raw material to a short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 200°C to 250°C and with the condenser of that column at a temperature between 80°C to 120°C to form a distillate weighing between 70% to 90% in weight per weight of the raw material fed.

(b) collecting the distillate as wax essentially free of pitch

(c) a short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters

(d) a residence time in the column for the feed material of less than 15 minutes

27. A method for producing a free sterol compound according to claim 26 CHARACTERIZED because it includes:

(a) mixing the distillate collected in stage (b) or part of that distillate with an organic solvent

(b) heating or refluxing the stage (a) mixture

(c) cooling the stage (b) mixture to a temperature of –20 to 20°C

(d) separating the solids from the stage (c) mother liquor

(e) desolventizing the stage (d) solids

(f) collecting the stage (e) solids

28. The method according to claim 27 CHARACTERIZED because the solvent in stage (a) is acetone, methyl ethyl ketone or any dialkyl ketone containing between 3 to 10 carbon atoms, methanol or ethanol or any aliphatic alcohol with 1 to 6 carbon atoms or a mixture of any of two or more of such solvents.

29. The method according to claim 27 or 28 CHARACTERIZED because the sterol compound contains at least 90% in weight of free sterols or stanols

30. A method for producing a fatty alcohol concentrate according to claim 26 CHARACTERIZED because it includes:

(a) mixing the distillate collected in stage (b) or part of that distillate with an organic solvent

(b) heating or refluxing the stage (a) mixture

(c) cooling the boiled mixture to a temperature of –20 to 20°C or less

(d) separating the mother liquor from the solids produced in stage (c)

(e) desolventizing the stage (d) mother liquor

(f) mixing the solids produced in stage (e) with an organic solvent

(g) heating or refluxing the stage (f) mixture

(h) cooling the mixture boiled in stage (g) to a temperature of –20 to 20°C or less

(i) separating the stage (h) solids

(j) desolventizing the stage (i) solids

31. The method according to claim 30 CHARACTERIZED because the stage (a) solvent is acetone, methyl ethyl ketone or any dialkyl ketone containing between 3 to 10 carbon atoms, methanol or ethanol or any aliphatic alcohol with 1 to 6 carbon atoms or a mixture of any of two or more of such solvents.

32. The method according to claim 31 CHARACTERIZED because the stage (f) solvent is hexane, heptane, toluene or xylene or a mixture of any of two or more of such solvents.

33. The method according to claim 29, 30 or 32 CHARACTERIZED because the fatty alcohol concentrate contains at least 50% in weight of docosanol or tetracosanol.

34. A method for separating components of a raw material containing neutral black-liquor soap compounds CHARACTERIZED because it includes:

(a) feeding the raw material to a short path distillation column at a pressure between 0.01 to 5 mbar, with the column evaporator at a temperature between 100°C to 200°C and with the condenser of that column at a temperature between 60°C to 100°C to form a residue weighing between 45% to 65% in weight per weight of the raw material fed.

(b) collecting the residue as pitch and sterols essentially free of wax

(c) a short path distillation column with an evaporation surface and a condensation surface separated by a distance no greater than 50 centimeters

(d) a residence time in the column for the feed material of less than 15 minutes

35. A method for producing a sterol compound according to claim 34 CHARACTERIZED because it includes:

(a) mixing the residue collected in stage (d) or a part of that residue with an organic solvent

(b) refluxing the stage (a) mixture

(c) cooling the stage (b) mixture to a temperature of –20 to 20°C

(d) separating the stage (c) solids

(e) desolventizing the stage (d) solids

(f) collecting the stage (3) solids

36. The method according to claim 35 CHARACTERIZED because the solvent in stage (a) is acetone, methyl ethyl ketone or any dialkyl ketone containing between 3 to 10 carbon atoms, methanol or ethanol or any aliphatic alcohol with 1 to 6 carbon atoms or a mixture of any of two or more of such solvents.

37. The method according to claim 35 or 36 CHARACTERIZED because the sterol compound contains at least 90% in eight of free sterols or stanols

38. A method for producing a compound of free sterols or stanols or fatty alcohols according to claim 34 CHARACTERIZED because it includes:

(a) mixing the residue collected in stage (b) or a part of that residue with an organic solvent

(b) heating or refluxing the stage (a) mixture

(c) cooling the boiled mixture to a temperature of –20 to 20°C

(d) separating the mother liquor from the stage (c) solids

(e) desolventizing the stage (d) mother liquor

(f) collecting the stage (e) solids

(h) [sic] mixing the stage (f) solids or a part of such solids with an aqueous or alcoholic sodium or potassium or ammonium hydroxide or pure ammonium solution and an organic solvent

(g) heating the mixture to a temperature between 100°C to 300°C for a sufficient time

(h) cooling the stage (b) mixture

(i) separating the organic phase of the stage (c) mixture

(j) mixing the stage (i) organic phase with water

(k) separating the organic phase and the water of stage (j)

(l) desolventizing the organic phase separated in stage (k)

(m) collecting the stage (l) solids

39. The method according to claim 38 CHARACTERIZED because the solvent in stage (a) is acetone, methyl ethyl ketone or any dialkyl ketone containing between 3 to 10 carbon atoms, methanol or ethanol or any aliphatic alcohol with 1 to 6 carbon atoms or a mixture of any two or more of such solvents.

40. The method according to claim 39 CHARACTERIZED because the stage (h) solvent is hexane, heptane, toluene or xylene or a mixture of any two or more of such solvents.

41. The method according to claim 38, 39, or 40 CHARACTERIZED because the compound of sterols or stanols or fatty alcohols contains no less than 50% in weight of free sterols or stanols or fatty alcohols.

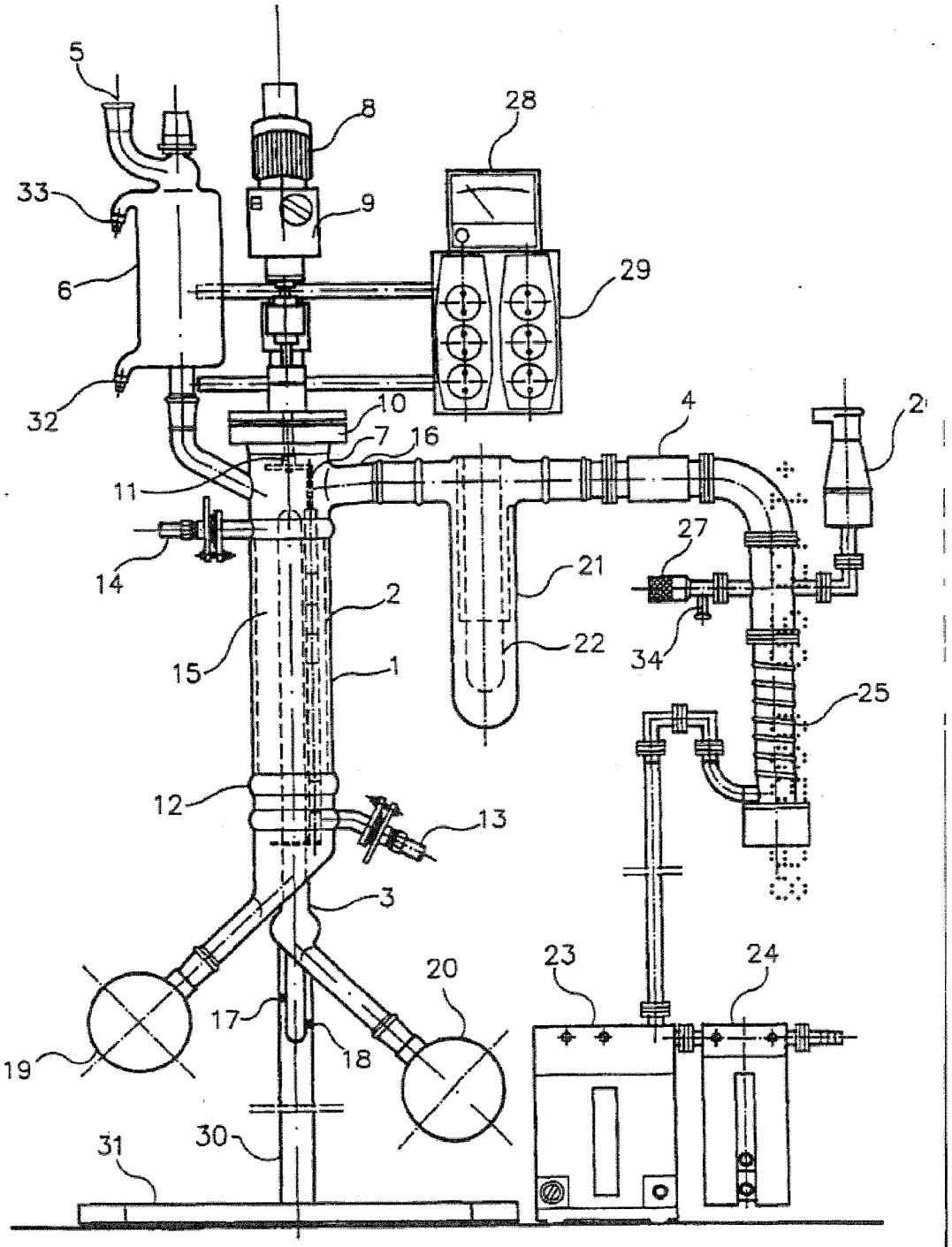
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Figure 1

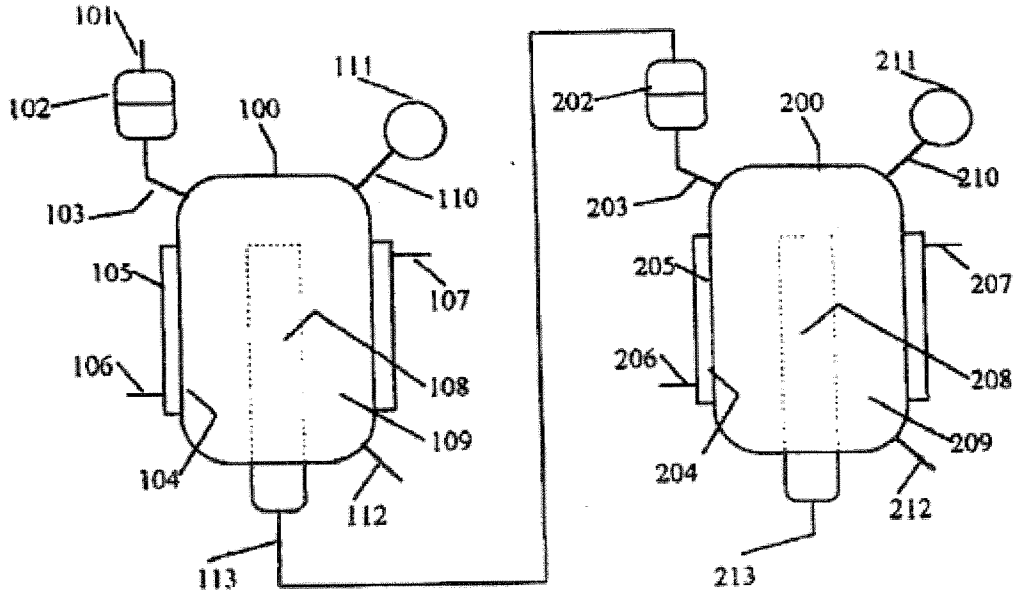

Figure 2

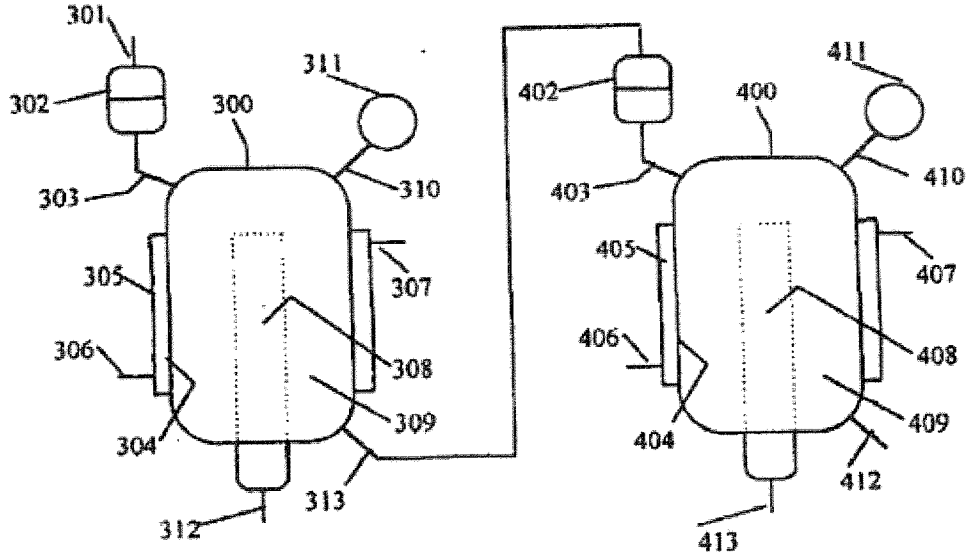

Figure 3